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Historical perspective

Towards predicting the stability of protein-stabilized emulsions

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ABSTRACT

The protein concentration is known to determine the stability against coalescence during formation of emulsions. Recently, it was observed that the protein concentration also influences the stability of formed emulsions against flocculation as a result of changes in the ionic strength. In both cases, the stability was postulated to be the result of a complete (i.e. saturated) coverage of the interface. By combining the current views on emulsion stability against coalescence and flocculation with new experimental data, an empiric model is established to predict emulsion stability based on protein molecular properties such as exposed hydrophobicity and charge. It was shown that besides protein concentration, the adsorbed layer (i.e. maximum adsorbed amount and interfacial area) dominates emulsion stability against coalescence and flocculation. Surprisingly, the emulsion stability was also affected by the adsorption rate. From these observations, it was concluded that a completely covered interface indeed ensures the stability of an emulsion against coalescence and flocculation. The contribution of adsorption rate and adsorbed amount on the stability of emulsions was combined in a surface coverage model. For this model, the adsorbed amount was predicted from the protein radius, surface charge and ionic strength. Moreover, the adsorption rate, which depends on the protein charge and exposed hydrophobicity, was approximated by the relative exposed hydrophobicity (Q_H). The model in the current state already showed good correspondence with the experimental data, and was furthermore shown to be applicable to describe data obtained from literature.

Contents

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1. Introduction

Proteins are widely used for the stabilization of emulsions [1–3]. The four main destabilization mechanisms affecting a protein-stabilized emulsion are creaming, coalescence, flocculation and Ostwald ripening [4]. During emulsion formation, proteins are typically considered to adsorb to the interface, and thereby stabilize the emulsion against coalescence [5]. After formation, the emulsion stability against flocculation is described to be determined by the charge of the adsorbed protein layer [4,6]. For oil-in-water emulsions destabilization by Ostwald ripening is often neglected, since typical triglyceride oils used in food emulsions, such as corn and peanut oil, have a low solubility in water [8–10] and can therefore not diffuse through the water phase.

Next, the link between coalescence and flocculation of emulsions and the protein molecular properties are reviewed. Based on this information and recent work, an empiric model is proposed that links the stability against coalescence and flocculation to the protein molecular properties such as size, charge and hydrophobicity.

1.1. Stability against coalescence

Coalescence is reported to be the main destabilization mechanism during emulsion formation [5]. During formation, droplets with a certain defined size ($d_{3,2,min}$) will be formed, depending on for instance power input, interfacial tension and mass density of the continuous phase [7]. If sufficient protein is present to cover the newly formed interface (i.e. emulsion droplet) completely, the droplets are considered to be stable ($d_{3,2} = d_{3,2,min}$) (Fig. 1A). A lack of protein in the continuous phase will lead to incomplete coverage of the interface. This in turn results in coalescence during formation, until an interfacial area (i.e. droplet size) is reached for which there is sufficient protein present (Fig. 1A). Coalescence can therefore be prevented by increasing the protein concentration in the continuous phase. This explains the two characteristic concentration regimes which are observed during emulsion formation (i.e. protein-poor and protein-rich regime) [2,11].

In the protein-poor regime (regime I), the droplet size ($d_{3,2}$) is equal to the minimal droplet size for which the complete interface can be (sufficiently) covered with protein, as described in Eq. (1) [11]. The maximum adsorbed amount (Γ_{max}) in this regime corresponds closely to that of a monolayer [2,12,13]. Consequently, if the droplet size, calculated from Eq. (1) [11], is plotted against protein concentration, different curves are obtained depending on volume fraction oil (Φ_{oil}) and Γ_{max} (Fig. 2A). Recently, the maximum adsorbed amount for a protein has recently been described to be influenced by its molecular properties (i.e. size and charge) and system conditions (i.e. ionic strength) [14], as was previously shown for hard-sphere colloids [15–17].

In the protein-rich regime (regime II), the droplet size is only affected by factors such as power input, interfacial tension and mass density of the continuous phase ($d_{3,2} = d_{3,2,min}$) (Eq. 2).

$$d_{3,2(I)} \approx \frac{6\Phi_{oil}\Gamma_{max}}{(1-\Phi_{oil})C} \quad (1)$$

$$d_{3,2(II)} = d_{3,2,min} \quad (2)$$

where Φ_{oil} is the volume fraction oil [−], Γ_{max} is the maximum adsorbed amount [mg m^{-2}] and C is the protein concentration [g L^{-1}].

Assuming the validity of Eqs. (1) and (2), all curves are expected to superimpose onto a single curve by correcting for the C, Φ_{oil} and Γ_{max} (Fig. 2B). In this curve one critical point (F_s) is identified, where all curves shift from the protein-poor to the protein-rich regime. Using this stability factor (i.e. F_s), the critical protein concentration (C_{cr})

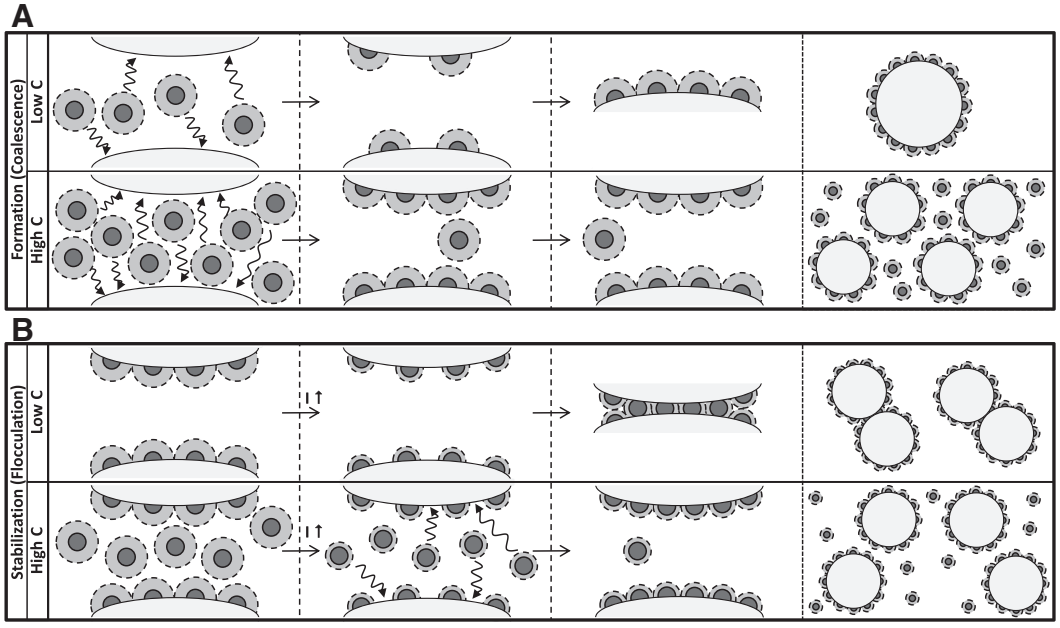

Fig. 1. Effect of low and high protein concentration on the emulsion stability against coalescence during formation (A) and against flocculation after formation (B). The dark and light grey circles represent the protein and the Debye screening length, respectively. The effective radius of an adsorbed protein is a combination of protein and the Debye screening length.